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SIMULATION STUDIES
FOR SURFACES AND MATERIALS STRENGTH

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16. Abstract

In this project computer simulation studies have been conducted to investigate materials properties. All the calculations have been carried out using atomic level simulation techniques which are based on semiempirical or model functions. During this project, functions with varying degrees of complexity have been derived and employed in simulations. Investigations include covalently bonded materials as well as systems involving metal atoms.

For small clusters calculated results provided information on various energy- and structure-related properties along with vibrational characteristics. Also, energy barriers for configurational transitions have been calculated for selected cases. Simulation calculations for surfaces produced new results in areas related to surface energies, reconstructions and relaxations, surface defects, surface stresses as well as adsorption and nucleation processes. Simulations have also been performed on bulk materials. Calculated results provided an atomic level understanding on energetics and structures of point defects, crystal stability, elastic properties and materials strength for various systems. Calculations involving polymeric materials include studies of polar polymer melts and polymer/solid interfaces. Simulations employing specially developed codes provided significant information about energetics and conformational characteristics of different polymeric chains.

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In this project computer simulation studies have been conducted to investigate materials properties. All the calculations have been carried out using atomic level simulation techniques which are based on semiempirical or model functions. During this project, functions with varying degrees of complexity have been derived and employed in simulations. Investigations include covalently bonded materials as well as systems involving metal atoms.

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This report covers simulation studies carried out to investigate various materials properties. All the investigations were conducted using atomic level simulation techniques based on parameterized semiempirical or model potential energy functions to describe atomic interactions.

During the course of this project, computer codes have been developed to implement various simulation methods such as static, molecular dynamics and Monte-Carlo. A new approach based on a Laplace-transform technique has been developed and used to derive thermodynamic expressions for Si systems (as averages of the appropriate microscopic dynamical functions) in molecular dynamics simulation studies [3]. Also, a number of potential energy functions have been developed and used to simulate a wide range of systems. In most cases, potential functions included two- and three-body terms to take into account many-body interactions. Parameters for model functions have been calculated based on experimental data on bulk and gas phase properties for systems containing C and Si [2,35] and Ga, As and AlAs species [37,38]. For systems with Al, Be and Cu atoms, high level ab initio results have been employed in the parameterization [18,20]. It has been shown that the choice of potential functions describing the system under consideration is an important issue in its transferability [33]. Several comparative investigations have been carried out to analyze applicability and limitations of potential functions for Si [27,40,41,42,47,50]

For small clusters calculations provided detailed structural, vibrational and energetics information [10,14], For metal clusters (such as Be Al and Cu), simulations based on model potentials provided results consistent with high level calculations [18,20]. Properties of small clusters have been reviewed and critically analyzed during this time [28,29]. Simulations produced reaction paths for configurational transformation of Al clusters [31,34]. For smaller and medium size clusters of carbon the validity of model functions has been demonstrated [40,41,42,50].

Simulation calculations for surfaces produced new results in areas related to surface energies, reconstructions and relaxations, surface defects, surface stresses as well as adsorption and nucleation processes. In this project three-body interactions have been used in simulation calculations for surfaces of Si systems for the first time. Calculated results revealed a wealth of atomic level information on surface relaxation and reconstruction [5,6,19], stress distribution [13], formation of kinks and ledges and their interactions [15,16,24], diffusion and interaction of adatoms with ledges [17], amorphous film formation [23,25], defect induced reconstruction [32] and binding sites for C atoms [52]. For systems involving C and Si atoms simulation calculations provided new results on the reconstruction of surfaces for diamond and β-SiC [4], and diffusion probabilities for C, Si and SiC species [6]. For systems with Ga, Al, As and Au atoms, simulations produced a better understanding about structural properties for surfaces and multilayer interfaces [7, 21,36], the role of the surface stress tensors on the reconstruction, nucleation and growth [22,43], adsorption [30] and cluster formation processes [26,45]. For surfaces of systems containing C atoms (i.e., for the low index planes of diamond), simulation calculations produced new results for surface energies, ledge energies, reconstruction and multilayer relaxations [39,44,51], formation of defects and growth processes [46,49].

For bulk systems simulations produced new results on crystal stabilities and elastic constants [5,8], the effect of pressure and temperature on phase transitions [9] and stability diagrams for crystalline phases [11], and structures of point defects [48]. Parametric studies have been conducted to analyze responses of materials to external forces to gain an atomic level understanding of materials strength. In these calculations, statics and molecular dynamics techniques have been employed to investigate slip and crack formation processes [1,12].

In general, computation of strictly thermal quantities for materials presents a challenge. Whereas the usual simulation methods allow the estimation of mechan-

ical properties such as energy, enthalpy and volume, they do not provide direct access to free energy. For low temperature applications enthalpy (or energy) values could be satisfactory for explaining various processes. At elevated temperatures, however, entropy contributions are not negligible. Therefore, simulations of thermodynamic quantities for systems at higher temperatures must provide free energy values. In our recent investigation [64] the cumulant expansion and the thermodynamic integration techniques, along with others, have been considered for electrically neutral point defect free energies of formation and migration in Si. The thermodynamic integration method was found to be best. Free energies, enthalpies and entropies of both formation and migration were evaluated as a function of temperature using available Si potential energy functions for a variety of different types of point defects. Equilibrium point defect population and diffusion coefficients have been evaluated as a function of temperature. Near the silicon melting temperature, the Frenkel defect formation process was simulated and no activation barrier has been found for point defect recombination.

Investigations for polymeric materials have been conducted employing molecular dynamics procedures based on parameterized force field models. In all cases, parameters were obtained from ab initio electronic calculations for energetics and structures of prototype molecules. In these studies the validity of the simulations for molecular configurations has been demonstrated by comparing the calculated results with experimental data. Calculations for polyethylene, the polymer/solid surface and the melt systems reproduced local dynamics consistent with experiments [55,57].

Simulation calculations for polymers and related model molecules provided significant new information about the conformational characteristics for atactic poly(vinyl chloride) melts [53], 2,4-dichloropentane and 2,4,6-trichloroheptane [54], 1,2-dimethoxyethane [59,62], as well as for polymer melts between parallel surfaces [58], poly(oxymethylene) [61,62] and poly(tetrafluoroethylene) chains

[63]. Also, equilibrium and dynamic properties of polymethylene melts confined between solid surfaces have been simulated to understand the influence of surface and interfacial properties [56,57]. Calculations based on a third-order rotational isomeric state model for poly(oxyethylene) resulted in significant insight into the conformational characteristics of poly(oxyethylene) [60].

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